UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

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MEMORANDUM

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

SUBJECT: Pyrethrin residue chemistry data call-in. Photolysis data submitted by Chemical Specialties Manufacturures Association (CSMA).

MRID No. 407004-00. RCB No. 4222.

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Background

As discussed in a recent memo (R. Loranger, memo of 1/22/88), the Pyrethrum Task Force submitted a "Working Document for: PATHWAYS FOR BREAKDOWN AND METABOLISM OF NATURAL PYRETHRINS", dated 6/19/87. The document included data from a photodegradation study conducted in 1987. In that study, an acetone solution of Task Force blend FEK-99 (a blend of pyrethrins manufactured by three companies) was evaporated in petri dishes to give films having a known weight to unit area. The films were exposed to sunlight for various periods of time and analyzed by GC-EC for pyrethrin content. The results demonstrated that pyrethrins are rapidly degraded by light with a half life of about 10 minutes. No degradates were identfied.

In a subsequent submission (7/27/87), a similar experiment was carried out by Fairfield American Corp. Films of FEK-99 were prepared as before. One Petri dish was exposed to sunlight for 4 hours. The plate was then washed with acetone and the washings injected into a GC equipped with a flame ionization detector. Submitted chromatograms (page 26 of the present submission) show that the film extract not exposed to direct sunlight possesses the usual profile of pyrethrins. Peaks are well resolved except for a small broadening due to heat-generated isomers which are usually encountered in GC. The extract from the film exposed to

sunlight shows "a jagged 'mound' of multiple peaks which are not separated but run into one another". The Pyrethrum Task Force concluded that "[t]here is no known way in which we can separate or attempt to monitor the decomposition product of pyrethrum extract in such a complex mixture of photolytic products". We concurred with that assessment (R. Loranger, memo of 8/15/88).

In our 1/22/88 memo, we advised the Task Force to devise a protocol for a more detailed glass plate experiment which would include identification of the degradates.

In response, the registrants submitted results of analyses by Shrader Laboratories of the acetone washings from the petri dishes. Conclusions from Shrader Labs.' report were reviewed in our 8/15/88 memo (R. Loranger), but the complete report had not been submitted at that time. Shrader Labs.' conclusions were the following:

1. Of the materials that could be gas-chromatographed, the bulk of the sample was palmitic acid.

2. The terpene and alkane fractions of the pyrethrin mixture were not detectable.

3. The active pyrethrins degraded to chrysanthemum monocarboxylic acid and chrysanthemum dicarboxylic acid.

4. A complex mixture of isomerized pyrethrins was present.

The registrants concluded that photolysis of pyrethrin films results in a complex mixture which is not capable of being separated, quantified or monitored with the current state of instruments and knowledge.

In our 8/15/88 review we concluded the following:

1. Submitted data indicate that of the six active ingredients, the two pyrethrins disappear significantly faster than the cinerins and jasmolins.

2. The chromatograms of the pyrethrin film exposed to four hours of sunlight showed a "jagged 'mound' of multiple peaks which are not separated but run into another" [registrants' words], i.e., the active ingredients degrade rapidly to numerous components which cannot be identified, let alone quantified. [This conclusion was based on the earlier GC-FID chromatograms discussed above. We had not yet seen chromatograms from the GC/MS analyses.]

3. The HED Metabolism Committee should address the need for a radiolabeled study or studies. Issues that should be

addressed are:

a. Applicability of glass plate studies to residues on crops.

b. Components of the residue that should be regulated.

c. TOX concern over the possible presence of photodegradates that are not animal metabolites.

The present submission is the complete report of Shrader Labs' pyrethrin photolysis experiments.

Conclusion

The submitted data do not support our previous (tentative) conclusion that the regulation of all the individual pyrethrins plus their degradates is not feasible. The GC/MS data clearly show that the major pyrethrin constituents after photolysis of a film on a glass plate are cis-chrysanthemic acid, chrysanthemum dicarboxylic acid, cinerin I and II's, jasmolin I and II's and isomers of these four pyrethrins. Pyrethrin I and II's are not present in significant amounts.

Recommendation

We modify our deferral (expressed in our 8/15/88 memo, pp. 3-4) to the HED Metabolism Committee. The Committee should determine whether regulation of all the individual pyrethrins, including their photolytic degradates is necessary or desirable. Our deferral should read as follows:

> Are the results of glass plate studies showing rapid degradation of pyrethrins applicable to residues on crops?
>
> If the answer to the above is yes, is it necessary to regulate all the identified pyrethrins and their degradates. If not all which, if any, of the identified degradates should be regulated?
>
> Is Toxicology Branch concerned with the possible presence of photodegradates that are <u>not</u> animal metabolites?

Detailed Considerations

CSMA has submitted the following report:

G.S. Reddy, "Analytical Results of Pyrethrin Photolysis Residues After Exposure to Natural Sunlight", 3/10/88, Laboratory Project ID (Shrader Labs.) SL# 15981-15982. (MRID No. 407004-00)

As in previous experiments pyrethrin film was exposed to sunlight for 4 hours. Acetone washings taken from film before and after exposure were analyzed by GC/MS. A 30 m DB-5 capillary column was temperature programmed from 50-300°C at 8°C per minute. The total ion current (TIC) chromatogram of the unphotolyzed sample, FEN-9, is identical to that of FEK-99, the blend of various manufacturers' refined pyrethrin concentrates. Chromatograms from samples of FEN-9 and FEK-99 are shown on pp 7-8 and 32-33, respectively.

Not surprisingly, the corresponding photolyzed sample, FEN-10, is quite different. The chromatograms corroborate the preliminary conclusions:

> The hydrocarbon fraction is missing. (The registrants have still not provided evidence that this fraction is due to solvent.)
>
> The terpene fraction is missing.
>
> The major constituent of FEN-10 is palmitic acid. In FEN-9 and FEK-99 the major constituent or, more correctly, the constituent having the greatest peak height is cinerin I. [The peaks due to pyrethrin I and pyrethrin II show evidence of extensive decomposition in the GC.]
>
> Two low molecular weight pyrethrum decomposition products are observed in FEN-10: cis-chrysanthemic carboxylic acid and chrysanthemum dicarboxylic acid.
>
> The pyrethrum area of the chromatogram reveals a complex mixture consisting of cinerin I and II, jasmolin I and II and isomers of all four compounds. The pyrethrin I and II components are missing.

Identified pyrethrum components are given in Table I, below. Total ion currents for the peaks are also listed, but these should be approached with some caution. Response factors have not been given, and peak areas alone will not yield accurate concentrations.

Of the pyrethrins present, cinerin I and its isomer are the two constituents having greatest peak height. About 13 resolvable peaks appear in the pyrethrin region, ten of which have been identified. One is not a pyrethrin -- butyl benzyl phthalate, $C_4H_9OOCC_6H_4COOC_7H_7$, a common plasticizer regulated for food contact applications. This latter compound was not identified in the FEN-9 chromatogram but would probably have been masked by the thermal decomposition products from pyrethrin I if it were present.

<u>The resolution using GC/MS is far better than that of the</u>

earlier GC/FID analysis, which truly showed a "jagged mound of multiple peaks". The GC/FID analysis utilized a 2 m column of 3 mm i.d. packed with W-AP support and having liquid phase OV-225. Resolution with such packed columns is far lower than corresponding resolution with the capillary column of Shrader Labs' analyses. Assuming that the instrumental parameters for the FEN-9 and FEN-10 analyses were identical -- both analyses were run on the same day -- we also can conclude that the total concentrations of cinerins and jasmolins have declined, even though isomers were formed.

Table I

Pyrethrum Components of FEN-9 and FEN-10

Pyrethrin-Related Component	TIC FEN-9	TIC FEN-10
cis-Chrysanthemic Acid		2,520
Chrysanthemic Dicarboxylic Acid		2,992
Cinerin I	38,560	9,648
Cinerin I Isomer		7,808
Unidentified		3,240
Jasmolin I	22,864	5,264
Jasmolin I Isomer		5,448
Butyl Benzyl Phthalate		6,064
Cinerin II Isomer		3,144
Cinerin II	33,136	4,896
Cinerin II Isomer		4,400
Jasmolin II	16,592	3,400
Jasmolin II Isomer		2,616
Unidentified		2,704
Unidentified		3,200

Comment

We must slightly modify our deferral to the HED Metabolism Committee, for it is now clear that regulation of individual pyrethrins plus their degradates is feasible, provided that the

results of the glass plate studies are applicable to crops. Whether it is desirable is an issue the the Committee will have to resolve.

The particular isomers of cinerin and jasmolin have not been identified but are likely cis-trans or ester rearrangement isomers. Identification could be achieved in principle but would likely involve synthesis of the possible isomers.

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